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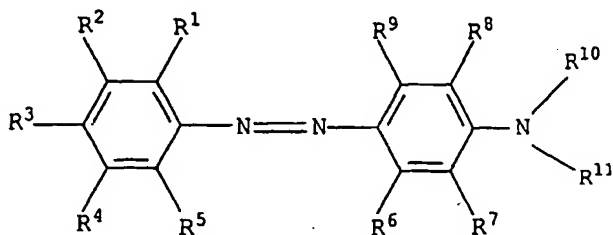
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(54) Title: OIL COMPOSITION AND METHOD OF DETECTING A MARKER IN AN OIL COMPOSITION



(IV)

(57) Abstract: Oil composition comprising a major amount of a natural and/or synthetic base oil and, as a marking substance, a detectable level of one or more compounds of formula (IV), and a method for detecting the presence of a marking substance in an oil composition, wherein the oil composition is contacted with a test strip comprising an acidic compound supported thereon, such

that said marking substance gives a colour reaction upon contact with the test strip.

OIL COMPOSITION AND METHOD OF DETECTING A MARKER IN AN  
OIL COMPOSITION

The present invention relates to an oil composition and a method of detecting a marker in an oil composition.

Adulteration, counterfeiting and other fraudulent activities in relation to oil compositions has been a  
5 concern in industry in recent years.

Such activities can result in lost revenue and lack of customer confidence.

Strategies to combat such fraudulent activities include the addition of dyes and/or covert chemical  
10 compounds (markers) to the oil composition.

The use of a dye or marker allows the authenticity of an oil composition to be assessed. This has many benefits for the oil composition manufacturer, including protection of brand name, increased customer confidence  
15 and tracking of product at any stage in the production and distribution chain.

In combating fraudulent activity, rather than using a simple dye, it is often desirable to employ a so-called  
20 silent marker, that is to say, a marker which imparts substantially no colour to an oil composition at the level at which it is used, but which can be easily detected, qualitatively or quantitatively, in the tagged oil composition by performing chemical and/or physical tests thereon. It is often preferable that such testing  
25 can be conducted in the field and markers are therefore usually detected by a reactive extraction method.

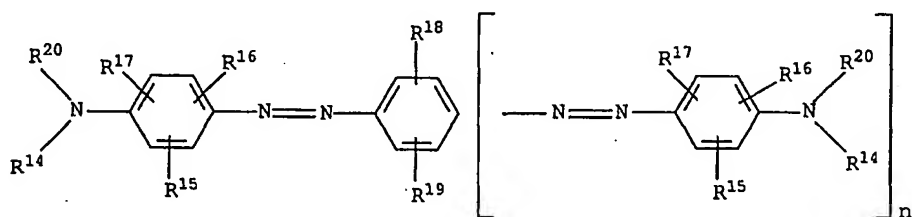
For example, US-A-5490872 discloses markers which are detectable by extraction from petroleum fuel with a

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dilute acidic solution such as a 10% hydrochloric acid or formic acid solution.

US-A-5560855 describes a method for tagging and identifying refrigeration lubricants using silent markers. Identification relies upon a reactive extraction method.

US-A-5145573 describes marked mineral oils containing, as marking substances, azo dyes of formula (I),



(I)

in which  $n$  is equal to 0 or 1,  $\text{R}^{14}$  and  $\text{R}^{20}$  are the same or different and independently denote hydrogen or  $\text{C}_1\text{-C}_8$  alkyl optionally substituted by hydroxy and optionally interrupted by one or two oxygen atoms,  $\text{R}^{15}$  and  $\text{R}^{18}$  are the same or different and independently denote hydrogen,  $\text{C}_1\text{-C}_4$  alkyl or the radical  $\text{NR}^{13}\text{R}^{14}$ , in which  $\text{R}^{13}$  and  $\text{R}^{14}$  have the above meanings,  $\text{R}^{16}$ ,  $\text{R}^{17}$  and  $\text{R}^{19}$  are the same or different and independently denote hydrogen or  $\text{C}_1\text{-C}_4$  alkyl.

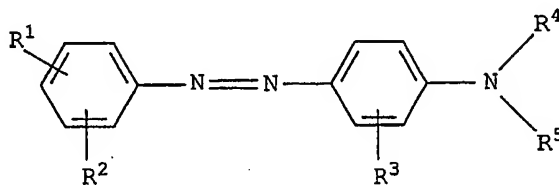
Markers of formula (I) have dye characteristics and additionally undergo a bathochromic shift of their absorption maximum and an increase in absorbance when there is added thereto a protogenic acid.

The marked mineral oil of US-A-5145573 is tested by shaking a sample of the oil with a detector reagent comprising a protogenic acid, separating the two phases and comparing colorimetrically the coloured phase with a

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solution of known concentration, so that the dye content can be assessed quantitatively.

US-A-5182372 discloses mineral oils containing one or more azo dyes of formula (II),

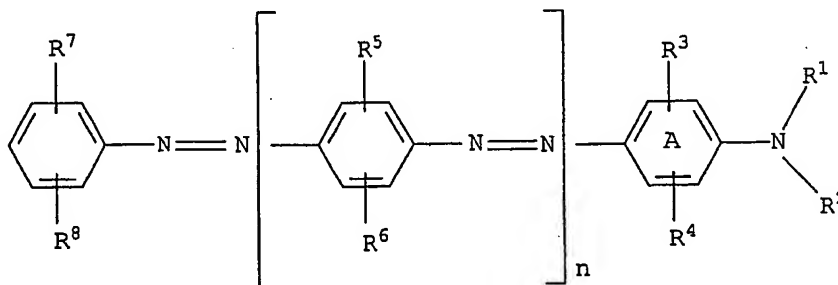


(II)

in which  $R^1$ ,  $R^2$  and  $R^3$  are the same or different and independently denote hydrogen,  $C_1$ - $C_4$  alkyl or  $C_1$ - $C_4$  alkoxy,  $R^4$  denotes  $C_1$ - $C_6$  alkyl and  $R^5$  denotes  $C_2$ - $C_8$  alkyl which is substituted by hydroxy and may be interrupted by 1, 2 or 3 oxygen atoms, provided that the total number of carbon atoms in the radicals  $R^4$  and  $R^5$  is at least 5.

The indication of the dyes of formula (II) in said mineral oils is achieved by testing the oil with aqueous acid to obtain a colour reaction.

US-A-5827332 describes hydrocarbons containing, as pH-dependent markers, azo dyes of formula (III),



(III)

where the ring A may be benzofused,  $n$  is 0 or 1,  $R^1$  is hydrogen or  $C_1$ - $C_{15}$  alkyl which may be interrupted by from 1 to 4 ether oxygen atoms,  $R^2$  is  $C_1$ - $C_{15}$  alkyl which

may be interrupted by from 1 to 4 ether oxygen atoms, or a radical of the formula  $L-NX^1X^2$ , where L is  $C_2-C_8$  alkylene and  $X^1$  and  $X^2$  independently of one another are each  $C_1-C_6$  alkyl or, together with the nitrogen atom  
5 linking them, form a 5-membered or 6-membered saturated heterocyclic radical which may furthermore contain an oxygen atom in the ring,  $R^3$ ,  $R^4$ ,  $R^5$ ,  $R^6$ ,  $R^7$  independently of one another are each hydrogen,  $C_1-C_{15}$  alkyl or  $C_1-C_{15}$  alkoxy and  $R^8$  is hydrogen,  $C_1-C_{15}$  alkyl,  $C_1-C_{15}$  alkoxy,  
10 cyano, nitro or a radical of the formula  $COOX^3$ , where  $X^3$  is hydrogen,  $C_1-C_{15}$  alkyl which may be interrupted by from 1 to 4 ether oxygen atoms, or is a radical of the formula  $L-NX^1X^2$ , where L,  $X^1$  and  $X^2$  each have the above meanings.

15 Azo dyes of formula (III) are said to give a colour reaction, i.e. a colour change, accompanied by a deepening of colour, under action of a protic acid.

Testing of the tagged hydrocarbon is said to occur by extracting an amount thereof with an amount of aqueous  
20 alcoholic or alcoholic solution of the protic acid.

Reactive extraction methods present a number of problems. Said methods often give rise to handling difficulties in the field as they involve reagents which may leak or spill, and which are often highly  
25 concentrated acidic solutions. Furthermore, testing is wasteful as sampled oils are contaminated and cannot be returned to the bulk oil. Thus, such methods also present disposal problems for the reagents used and the samples tested.

30 A further problem is that extractive testing methods require a clear, homogeneous phase separation, which can often be a slow process.

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5 An alternative method that has been suggested in EP-A-0887644 is to draw a fuel composition comprising an acid- or base- extractable marker through an ion-exchange resin column which is acidic or basic, as the case may be.

10 It is highly desirable to develop further alternatives for testing marked oil compositions which not only avoid the problems presented by reactive extraction methods, but which are also inexpensive, fast, and simple in that they require no special equipment or skills in order to perform and which can therefore be carried out in the field..

15 It is particularly attractive to be able to develop a method which can be carried out by the end customer at the point of sale, thereby increasing customer confidence in the authenticity of the product that they are purchasing.

20 A further difficulty in developing such a method that can be carried out by unskilled operators is that often oil compositions may have some inherent colouration due to the presence of certain additives and/or contaminants therein.

25 For example, the aromatics content of a base oil may lead to a yellow-orange colouration thereof and thus compositions comprising said base oil therein may have an inherent colouration. Such an inherent colouration may present difficulties in detecting a marker therein when said marker undergoes a colour change upon testing. For example, the colour change of a marker which generally changes to from colourless/yellow to red upon action of an acid may not be easily detected if there is a yellow-orange background colouration to the oil composition. Such a colour change may then only be presented as a deepening in the yellow-orange colouration.

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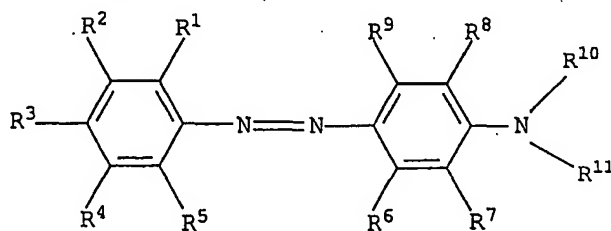
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Thus, it is of importance to not only develop a method which overcomes the problems of reactive extraction methods, but to also find a marking substance that may be used in oil compositions which gives a clear and unambiguous colour change even when the oil composition has an inherent colouration, such that the colour change can be detected by an unskilled operator.

There has been surprisingly found in the present invention a simple, fast and economic method for detecting the presence of marking substances in oil compositions which can be carried out by unskilled operators in the field.

In addition, there has also been found in the present invention a marking substance which gives a clear and unambiguous colour change in an oil composition under action of an acidic compound that can be easily detected by unskilled operators, even when said oil composition has some inherent colouration.

The present invention provides an oil composition comprising a major amount of a natural and/or synthetic base oil and, as a marking substance, a detectable level of one or more compounds of formula IV,



(IV)

wherein R<sup>1</sup> - R<sup>9</sup> are the same or different and are independently chosen from hydrogen, C<sub>1-15</sub> alkyl and other non-conjugated groups; R<sup>10</sup> is chosen from hydrogen and C<sub>1-15</sub> alkyl; and R<sup>11</sup> is a conjugated group.

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The present invention further provides a method for detecting the presence of a marking substance in an oil composition which comprises a major amount of a natural and/or synthetic base oil and a detectable amount level  
5 of a marking substance, wherein the oil composition is contacted with a test strip comprising an acidic compound supported thereon, such that said marking substance gives a colour reaction upon contact with the test strip.

Generally, said colour reaction will be apparent by  
10 a colour change on the portion of the test strip which is contacted with said oil composition.

Also provided by the present invention is a test strip comprising an acidic compound supported thereon.

By "conjugated group" in the present invention is  
15 meant a group,  $R^{11}$ , which is conjugated through the adjacent nitrogen atom to which  $R^{10}$  is also bonded, to the azo part of the molecule under action of an acidic compound, thereby shifting the value of  $\lambda_{max}$  for the marking substance as a whole to above 485 nm, preferably  
20 above 495 nm, provided that said group does not increase  $\lambda_{max}$  for the marking substance as a whole in its basic state to wavelengths of higher than 485 nm, preferably than 475 nm.

In a preferred embodiment,  $R^{11}$  is a group selected  
25 from  $-CX=CYZ$ , wherein X is chosen from hydrogen,  $C_{1-8}$  alkyl, alcohol, ether, acid, amine, aldehyde, nitro and halide, in particular  $-Cl$ ; Y is hydrogen or an ethylenically saturated or unsaturated hydrocarbyl group containing from 1 to 6 carbon atoms; and Z is hydrogen,  
30  $C_{1-8}$  alkyl, alcohol, ether, acid, amine, aldehyde, nitro and halide, in particular  $-Cl$  or X and Y together form an ethylenically saturated or unsaturated bivalent group containing 3 to 5 carbon atoms in the backbone thereof,



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said bivalent group optionally containing one or more heteroatoms therein.

5 R<sup>11</sup> may contain heteroatoms and in a preferred embodiment is selected from an optionally substituted conjugated olefinic group containing from 2 to 8 carbon atoms in the olefin backbone of the group, an optionally substituted aromatic group, an optionally substituted polyaromatic group, an optionally substituted aromatic heterocyclic group and an optionally substituted  
10 polyaromatic heterocyclic group.

Examples of optionally substituted aromatic groups and optionally substituted polyaromatic groups include phenyl, naphthyl, anthracenyl, phenanthracenyl.

15 Examples of optionally substituted aromatic heterocyclic groups and optionally substituted polyaromatic heterocyclic groups include 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, furyl, thienyl, indenyl, imidazolyl, triazolyl, oxazolyl, isoxazolyl, carbazolyl, thiazolyl, benzothiazolyl, thiadiazolyl, pyrimidinyl,  
20 pyridyl and pyridazinyl.

Said groups may be optionally substituted with one or more groups such as C<sub>1-8</sub> alkyl, alcohol, ether, acid, amine, aldehyde, nitro and halide, in particular -Cl.

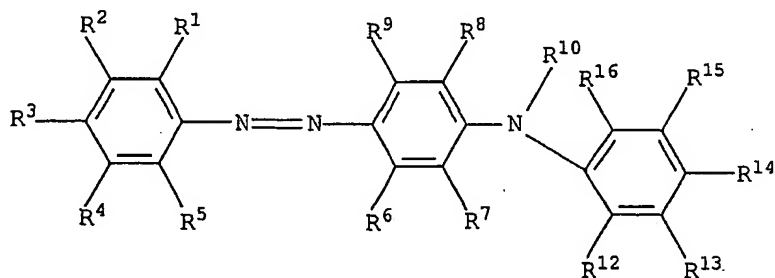
25 By "non-conjugated group" in the present invention is meant a group which does not shift the value of  $\lambda_{\max}$  for the marking substance as a whole in its basic state to wavelengths of higher than 485 nm, preferably than 475 nm.

30 Non-conjugated groups that may be conveniently used include halide, hydroxy, ether, sulphonic acid, carboxylic acid or alkenyl groups wherein the double bond therein is not directly conjugated to the aryl ring.

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In a preferred embodiment,  $R^1 - R^9$  in (IV) are the same or different and are independently chosen from hydrogen,  $C_{1-8}$  alkyl and other non-conjugated groups; and  $R^{10}$  is chosen from hydrogen and  $C_{1-8}$  alkyl.

5 In a preferred embodiment of the present invention, the marking substance is one or more compounds of formula V,



(V)

10 wherein  $R^1 - R^9$  are the same or different and are independently chosen from hydrogen,  $C_{1-15}$  alkyl and other non-conjugated groups;  $R^{10}$  is chosen from hydrogen and  $C_{1-15}$  alkyl; and  $R^{12} - R^{16}$  are the same or different and are independently chosen from hydrogen,  $C_{1-15}$  alkyl and  
 15 other non-conjugated groups.

In a preferred embodiment,  $R^1 - R^9$  in (V) are the same or different and are independently chosen from hydrogen,  $C_{1-8}$  alkyl and other non-conjugated groups;  $R^{10}$  is independently chosen from hydrogen,  $C_{1-8}$  alkyl; and  
 20  $R^{12} - R^{16}$  are the same or different and are independently chosen from hydrogen,  $C_{1-8}$  alkyl and other non-conjugated groups.

A particularly preferred marking substance according to the present invention is 4-(phenylazo)diphenylamine.

25 The general preparation of azo dyes by diazotization and coupling is well known in the art (see for example,

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Kirk-Othmer Encyclopaedia of Chemical Technology (3<sup>rd</sup> Edition, New York, 1978), Volume 3, pp 387-392).

5 The marking substances of formulae (IV) and (V) may be conveniently prepared by methods described therein and also in GB-B-1311374, US-A-5182372, US-A-5827332, or by methods analogous thereto.

10 The N-mono or di-substituted anilines which may be used in the preparation of said azo dyes are well known in the art and may conveniently be prepared by conventional methods, for example, by the reaction of aniline or N-monosubstituted aniline with alkyl halide (e.g. as described in Organic Chemistry, J. McMurry, Brooks/Cole Publishing Company, California, 1988, pp. 906-908 and J. Am. Chem. Soc. 82, 6163 (1960)); catalytic  
15 reduction of a Schiff's base formed from aniline and an aldehyde (e.g. as described in Org. React. 5, 301 (1940); reaction of aniline with the corresponding alcohol, such as phenol, in the presence of zinc chloride (Organic Chemistry. Volume One. The Fundamental Principles (4<sup>th</sup> Ed.), I.L. Finar, Longmans, London, 1963, page 567); and  
20 reaction of an aldehyde or ketone with an amine (e.g. as described in Arm. Khim. Zh. (1969), 22(8), 702-6 and Organic Chemistry, J. McMurry, Brooks/Cole Publishing Company, California, 1988, page 677).

25 The oil composition according to the present invention may conveniently comprise the marking substance in an amount in the range of from 1 to 400 ppmw, preferably in the range of from 5 to 100 ppmw and most preferably in the range of from 10 to 30 ppmw, based on  
30 the total weight of the oil composition.

The base oil used in the present invention is a natural or a synthetic base oil, or a mixture thereof. Said base oil may be conveniently used in fuel and/or lubricating oil compositions.

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The amount of base oil incorporated in the oil composition will depend upon the application in which it is intended to be used.

5 In fuel oil compositions, said base oil is preferably present in the oil composition in an amount in the range of from 60 to 99.95 % wt., more preferably in an amount in the range of from 65 to 99 % wt., with respect to the total weight of the oil composition.

10 In lubricating oil compositions, said base oil is preferably present in the oil composition in an amount in the range of from 60 to 99.95 % wt., more preferably in an amount in the range of from 90 to 99.95 % wt., with respect to the total weight of the oil composition.

15 Liquid hydrocarbon fuel oils include gasolines, kerosines, jet fuels, diesel fuels, heating oils and heavy fuel oils. Such fuel oils may consist substantially of hydrocarbons or they may contain blending components, such as alcohols or ethers.

20 Liquid hydrocarbon fuel oils of the gasoline boiling range are typically mixtures of hydrocarbons boiling in the temperature range from about 25°C to about 232°C, comprising mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons.

25 The base fuel oil is derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of  
30 these.

The hydrocarbon composition and octane level of the base fuel are not critical. The octane level,  $(R+M)/2$ , will generally be above about 85 (where R is Research Octane Number and M is Motor Octane Number).

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Liquid hydrocarbon fuel oils which are middle distillate fuel oils typically have a boiling range in the range 100°C to 500°C, e.g. 150°C to 400°C.

Petroleum-derived fuel oils may comprise atmospheric  
5 distillate or vacuum distillate, or cracked gas oil or a blend in any proportion of straight run and thermally and/or catalytically cracked distillates. Such fuel oils include kerosine, jet fuels, diesel fuels, heating oils and heavy fuel oils. In a preferred embodiment, the fuel  
10 oil is a diesel fuel.

Diesel fuels typically have initial distillation temperature about 160°C and final distillation temperature of 290-360°C, depending on fuel grade and use. Preferred diesel fuels are low-sulphur diesel  
15 fuels.

The fuel oil composition according to the present invention can contain further additives usually present in fuel oils, such as anti-static agents, pipeline drag reducers, flow improvers (e.g. ethylene/vinyl acetate  
20 copolymers or acrylate/maleic anhydride copolymers) and wax anti-settling agents (e.g. those commercially available under the Trade Marks "PARAFLOW" (ex Infineum International Ltd.), "DODIWAX" (ex Clariant GmbH).

Fuel oil compositions of the present invention may  
25 contain other additive components in addition to those already indicated. For example, a dispersant additive, e.g. a polyolefin substituted succinimide or succinamide of a polyamine, may be included. Such dispersant additives are described for example in UK Patent 960,493,  
30 EP-A-147 240, EP-A-482 253, EP-A-613 938, EP-A-557 561 and WO-A-98/42808. Such dispersant additives are preferably present in amounts in the range of from 10 to 400 ppmw, more preferably 40 to 200 ppmw, active matter based on the fuel oil composition.

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When the liquid hydrocarbon middle distillate fuel oil has a sulphur content of 500 ppmw or less, the fuel oil composition preferably additionally contains a lubricity enhancer in an amount in the range from 50 to 500 ppmw based on the fuel oil composition. Commercially available lubricity enhancers include those available as "EC 831" and "PARADYNE (trade mark) 655" ex Infineum, "HITEC" (trade mark) E 580 ex Ethyl Corporation and "VEKTRON" (trade mark) 6010 ex Infineum.

Further additive components which may be present include ignition improvers (cetane improvers) (e.g. 2-ethylhexyl nitrate, cyclohexyl nitrate, ditertiarybutyl peroxide and those disclosed in US Patent No. 4,208,190 (at Column 2, line 27 to Column 3, line 21); anti-rust agents (e.g. that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", a propane-1,2-diol semiester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid), reodorants, anti-wear additives; anti-oxidants (e.g. phenolics such as 2,6-di-tert-butylphenol, or phenylenediamines such as N,N'-di-sec-butyl-p-phenylenediamine); corrosion inhibitors; ashless detergents; anti-knock agents; dehazers; spark-aiders; valve-seat protection compounds; synthetic or mineral oil carrier fluids; anti-foaming agents and metal deactivators. A reodorant may be included, if desired.

The concentration of the ignition improver in the fuel is preferably in the range 0 to 600 ppmw, e.g. 300

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to 500 ppmw. Concentrations of other additives not yet specified are each preferably in the range 0 to 20 ppmw.

The lubricant base oils that may be used in the oil composition of the present invention, can be any base  
5 fluid which is suitable for use in lubricating oils. The base oil can be a natural or a synthetic lubricant base oil, or a mixture thereof.

The natural oil can be an animal oil or vegetable  
oil, such as lard oil or castor oil, or a mineral oil  
10 such as liquid petroleum oils and solvent treated or acid treated mineral lubricating oil of the paraffinic, naphthenic, or mixed paraffinic/naphthenic type which may be further refined by hydrocracking and hydrofinishing processes and/or dewaxing.

15 Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as polymerised and interpolymerised olefins.

A suitable base oil may contain poly-alpha-olefins, such as polydecene. Preferably, the base oil is a  
20 hydrocarbon base oil. More preferably, the base fluid is a mineral oil which contains less than 10 % wt. of aromatic compounds, preferably less than 5 % wt., measured according to DIN 51378. It is further preferred that the base oil contains less than 1.0 % wt. of  
25 sulphur, calculated as elemental sulphur, preferably less than 0.1 % wt., measured according to ASTM D 4045. Such mineral oils can be prepared by severe hydroprocessing. Preferably, the lubricating oil has a kinematic viscosity in the range of from 5 to 220 cSt at 40 °C, more  
30 preferably of from 10 to 200 cSt, most preferably of from 20 to 100 cSt.

The lubricating oil composition according to the present invention can contain further additives that are usually present in lubricating oils, such as pour point

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depressants, anti-foam agents and demulsifier. Pour point depressants generally are high molecular weight polymers such as alkylaromatic polymers and polymethacrylates. As anti-foam agents, silicone polymers and/or  
5 polymethacrylates are generally used. Demulsifiers which are generally applied are polyalkylene glycol ethers. Furthermore, further detergents such as sulphonates and phenates, metal deactivators, antioxidants such as phenolic compounds, diphenyl amines and phenyl naphthyl  
10 amines, ashless anti-wear agents and/or ashless dispersants, such as succinimides, can be present.

The oil compositions of the present invention may be conveniently prepared by dissolving the desired amount of the marking substance in a carrier fluid and then  
15 admixing the resulting solution with base oil. The carrier fluid may then optionally be removed from the oil composition by conventional means such as distillation. Carrier fluids that may be conveniently used include hydrocarbon, alcohol and ester solvents.

20 Compounds of formulae IV and V as described herein may be used as pH-dependent marking substances in the oil compositions of the present invention as they give a colour reaction under action of an acidic compound.

Said acidic compound may be a protic acid and/or a  
25 Lewis Acid. Preferably, said acidic compound is a protic acid.

The choice of acidic compound depends upon the marking substance being tested and the method being used. In a preferred embodiment, the pKa of the acidic compound  
30 is below 4.8.

Such acidic compounds include mineral and organic acids such as o- & p- bromoacetic acid, chloroacetic acid, chlorobenzoic acid, chlorobutyric acid, chloropropionic acid, chloropropinic acid, citric acid,



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cyano acetic acid, cyanobutyric acid, cyanophenylacetic acid, cyclopropane 1:1 dicarboxylic acid, dichloroacetyl acetic acid, dihydroxymalic acid, dihydroxytartaric acid, lutidinic acid, maleic acid, malonic acid, naphthalene  
5 sulphonic acid, o-, m- & p- nitrobenzoic acid, oxalic acid, quinolinic acid, trichloroacetic acid, 2,4,6-trihydroxybenzoic acid, 2,4,6-trinitrophenol, hydrochloric acid, sulphuric acid, 4-dodecylbenzene sulphonic acid (DBSA), picric acid, benzene sulphonic  
10 acid, acetic acid, nitric acid, and amino benzene sulphonic acid.

For tests in which a relatively rapid colour change is desired, acidic compounds which may be conveniently used are those with a pKa of less than 3.

15 Preferred acidic compounds are those with a pKa value of less than 2, such as trichloroacetic acid, hydrochloric acid, sulphuric acid, 4-dodecylbenzene sulphonic acid (DBSA), picric acid and benzene sulphonic acid.

20 Particularly preferred acidic compounds are 4-dodecylbenzene sulphonic acid (DBSA), sulphuric acid and hydrochloric acid.

The acidic compounds may be conveniently used in aqueous solution at a concentration in the range of from  
25 0.05 to 1.5 mol/dm<sup>3</sup>, preferably 0.15 to 0.6 mol/dm<sup>3</sup> and most preferably 0.25 to 0.4 mol/dm<sup>3</sup>.

However, in another embodiment of the present invention, said acidic compound is supported on a test strip.

30 Said test strip may be made of any solid material that is capable of supporting said acidic compound. As the test strip will undergo colour reaction in the presence of a pH-dependent marking substance, it is particularly preferred that said test strip is made from

a material which is white or lightly coloured and which is not adversely effected by the presence of said acidic compound.

Suitable materials are, for example, glass  
5 microfibre, sintered glass, cellulose, cellulose nitrate, cellulose acetate, finely woven fabrics or porous materials including cotton, polypropylene, nylon, wood, neutral or acidic minerals. Basic materials (such as  $\text{Al}_2\text{O}_3$ ) are not suitable.

10 Compounds such as silica gel are not sufficiently acidic to be used on the test strip as the acidic compound per se.

Depending upon the acid to be used in testing, it is within the skill of the skilled person to select  
15 appropriate material for the test strip.

The acidic compound may be optionally adsorbed onto a carrier prior to being supported on the test strip. Suitable carriers are non-basic, absorbent and light in colour, and may conveniently include silica gel,  
20 cellulose, cellulose nitrate, cellulose acetate.

Said acidic compounds may be conveniently supported on the test strip at a concentration in the range of from 0.0003 to 0.3  $\text{mmol}/\text{cm}^2$ , preferably from 0.0015 to 0.15  $\text{mmol}/\text{cm}^2$ , and most preferably from 0.003 to 0.03  
25  $\text{mmol}/\text{cm}^2$ , based on the area of the test strip.

In general, the test strip may comprise a narrow rectangular piece of the acidic compound-impregnated material as described above. In another embodiment, a smaller piece of such a test strip may be conveniently  
30 attached to a plastic-laminated material printed with appropriate instructions for use. The plastic lamination would enable the test strip to be wiped clean.

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In a further embodiment, the test strip may comprise a white plastic-laminated opaque window mask in order to shroud the acidic compound-impregnated test strip and to therefore enhance the appearance of the colour change upon contact with the marking substance.

The test strip may be conveniently located in a holder made of a durable material, for example, polypropylene.

In a specific embodiment, such a test strip holder could be specifically designed to enable dipping of the test strip into the sump of an engine, that is to say, said holder could conveniently be a very narrow unit containing therein the acidic compound impregnated test strip attached to a disposable or re-usable dip-stick.

In a preferred embodiment of the method of the present invention, the oil composition comprises a marking substance according to formula(e) IV and/or V as hereinbefore described.

The present invention will now be illustrated by the following Examples, which should not be regarded as limiting the scope of the present invention in any way.

#### EXAMPLES

##### Example 1 - Preparation of the test strip

Test strips were prepared by submerging the test strip material in a solution of DBSA in heptane for 2 seconds, draining for 2 seconds and drying at 60°C.

Experiments to determine the effect of DBSA concentration in solvent were carried out at 5%, 10%, 15% & 20% in n-heptane and optimised at about 10%.

Various materials were evaluated for suitability in the test strip for the consumer point of sale spot test.

Plastic thin layer chromatography (TLC) plates coated with a medium such as SiO<sub>2</sub> appeared to be ideal as a polar substrate that could support coating with acid.

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However, under certain operating conditions gentle scuffing of the test strip substrate easily removed the absorbant surface, causing a poor scuffy surface and little acidified media. The process of cutting the TLC plate material also induced cracking and media loss.

"Whatman" chromatography paper was found to be a very suitable medium for a spot test. This medium was scuff resistant, and could be easily cut to size giving a good finish.

The paper was tested in a variety of thicknesses and porosity. Tests showed that "Grade 4 CHR" gave optimal performance. The particular grade of paper was found to work with a variety of acids. However, hydrochloric acid was found to make the paper brittle. If desired to use a combination of hydrochloric acid with "Whatman" chromatography paper Grade "4 CHR", the impregnated paper may be conveniently supported on a solid material, such as wood or plastic, in order to overcome any fragility of the impregnated paper.

"Whatman" chromatography paper Grade "4 CHR" supporting DBSA at a concentration of  $\approx 0.002 \text{ g/cm}^2$  performed very well.

Example 2 - Effect of type of Acid on Colour change in the Spot Test

A variety of acids that could be used to promote a colour change were tested in the presence of a 15W50 synthetic oil containing 4-(phenylazo)diphenylamine marker therein doped at 30 ppm..

The selection of mineral and organic acids were impregnated at a concentration of approximately  $0.01 \text{ mmol/cm}^2$  onto a strip of "Whatman" chromatography paper (Grade "4 CHR") and allowed to dry according to the methodology described above in Example 1.

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In the case of acids that were solid at room temperature, the neat acid crystals (normally soft deformable material) were forced into the paper surface with a palette knife in order to give a uniform film of acid over the paper surface.

A drop of the 4-(phenylazo)diphenylamine-doped oil was placed on to the acidified paper and any resulting colour change was noted with time. The results are shown in Table 1.

Table 1 - Effect of Acid Type on Colour Change

Acid	Appearance		
	After 2 minutes	After 10 minutes	After 3 hours
Hydrochloric Acid	1	1	1
Sulphuric Acid	1	1	1
DBSA	1	1	1
Acetic Acid	0	0	1
Hexanoic Acid	0	0	0
Octanoic Acid	0	0	0
Decanoic Acid	0	0	0
Lauric Acid	0	0	0
Tridecanoic Acid	0	0	0
Tetradecanoic Acid	0	0	0
Pentadecanoic Acid	0	0	0
Hexadecanoic Acid	0	0	0
Heptadecanoic Acid	0	0	0
Octadecanoic Acid	0	0	0

(0 = no colour change; 1 = strong pink/purple colouration)

The results showed that DBSA and mineral acids promote a good colour change. Acetic acid (pKa~4.75) gave a reaction after 2-3 hours.

Example 3 - Concentration of marker

Oil compositions were prepared containing a range of concentrations of from 0 to 30 ppm of 4-(phenylazo)diphenylamine marker in 15W50 synthetic oil.

- 5 Strips of "Whatman" chromatography paper (Grade "4 CHR") were impregnated with a solution of 10% DBSA in n-heptane and were allowed to dry as described in Example 1.

- 10 A drop of each of the marker-doped oil compositions was placed on the DBSA-impregnated test strips and the resulting colour changes were observed after 2 minutes, 10 minutes and 5 hours. The results are shown in Table 2.

15 Table 2 - Effect of marker concentration

Conc. of Marker in oil, ppm	Appearance		
	After 2 minutes	After 10 minutes	After 5 hours
0	0	0	0
3	0	0	1
6	1	2	2
12	3	3	3
15	3	3	3
18	4	4	4
25	4	4	4
30	4	4	4

(0 = no colour change; 1 = very slight pink colouration; 2 = slight pink colouration; 3 = distinct pink colouration; 4 = strong pink/purple colouration)

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The results showed that after 2 minutes there was a very distinct colour change at marker concentrations of 18 ppm, 25 ppm and 30 ppm. Such concentrations are highly suitable for testing by the method of the present invention.

6 ppm was the lowest concentration of the tested marker that would indicate the presence of a colour change after 2 minutes. The colour change was very slight and could be missed by an untrained eye.

Although the testing method of the present invention is not primarily designed to be a quantitative tool, using the marker concentrations for this experiment (30 ppm for an undiluted oil composition) it may be possible to give a very approximate estimation of the percentage of genuine product present in an oil composition.

In the field, fraudulent use commonly involves dilution of genuine products to 25% or 33% of the original concentration. At such a diluted concentration of marking substance, the trained eye may also be able to distinguish a partially diluted oil composition from an undiluted oil composition by using the testing method of the present invention.

A strong pink / purple colouration is observed after 2 minutes with 18 ppm of marker.

Using a marker concentration of 30 ppm, it may also be possible to detect partial substitution of genuine product.

#### Example 4 - Dip test

A test was carried out to compare results of the method of the present invention on oil compositions comprising different marker systems, i.e. a 15W-50 synthetic engine oil composition doped with 4-(phenylazo) diphenylamine at 30 ppmw and a similar oil composition doped with "Sudan 455" marker (used as received ex. BASF)

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(not according to formula (IV) of the present invention) at 60 ppmw. Testing was also carried out on an analogous unmarked oil composition.

5 The oil compositions were spotted onto a "Whatman" chromatography paper (Grade "4 CHR") containing dodecyl benzene sulphonic acid (DBSA) at a concentration of 0.006 mmol/cm<sup>2</sup>.

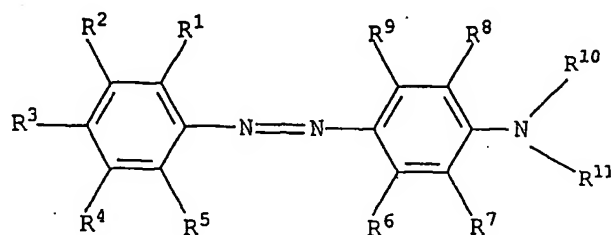
10 Individuals were asked in double blind tests to compare the colour quality of the spots formed on the test paper upon contact with each of the lubricant compositions.

15 In spite of the fact that the oil composition comprising "Sudan 455" marker therein was doped at twice the level of the 4-(phenylazo) diphenylamine-marked oil composition, 10 out of 10 people asked indicated that the spot which developed from 4-(phenylazo) diphenylamine-marked composition was the most distinctly different from that of the unmarked oil spot.



C L A I M S

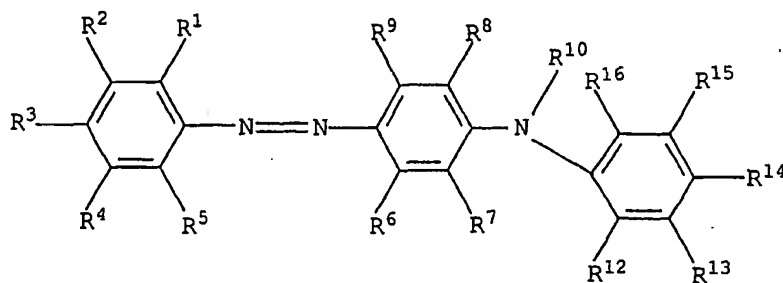
1. An oil composition comprising a major amount of a natural and/or synthetic base oil and, as a marking substance, a detectable level of one or more compounds of formula IV,



(IV)

5 wherein R<sup>1</sup> - R<sup>9</sup> are the same or different and are independently chosen from hydrogen, C<sub>1</sub>-15 alkyl and other non-conjugated groups; R<sup>10</sup> is chosen from hydrogen and C<sub>1</sub>-15 alkyl; and R<sup>11</sup> is a conjugated group.

10 2. Oil composition according to Claim 1, wherein said composition comprises, as a marking substance, a detectable level of one or more compounds of formula V,



(V)

wherein R<sup>1</sup> - R<sup>9</sup> are the same or different and are independently chosen from hydrogen, C<sub>1</sub>-15 alkyl and other

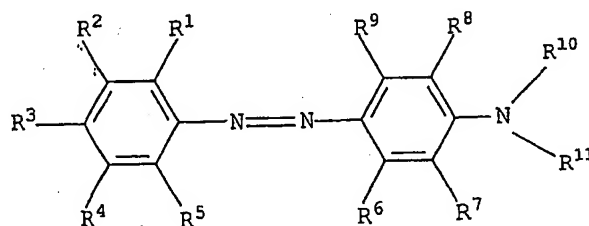
non-conjugated groups; R<sup>10</sup> is chosen from hydrogen and C<sub>1</sub>-15 alkyl; and R<sup>12</sup> - R<sup>16</sup> are the same or different and are independently chosen from hydrogen, C<sub>1</sub>-15 alkyl and other non-conjugated groups.

5 3. Oil composition according to Claim 1 or 2, wherein said composition comprises an amount in the range of from 1 to 400 ppmw of compounds of formulae IV and/or V, based on the total weight of the oil composition.

10 4. Oil composition according to any one of Claims 1 to 3, wherein said oil composition is a fuel oil composition.

5. Oil composition according to any one of Claims 1 to 3, wherein said oil composition is a lubricating oil composition.

15 6. Use of one or more compounds of formula IV,



(IV)

wherein R<sup>1</sup> - R<sup>9</sup> are the same or different and are independently chosen from hydrogen, C<sub>1</sub>-15 alkyl and other non-conjugated groups; R<sup>10</sup> is chosen from hydrogen and C<sub>1</sub>-15 alkyl; and R<sup>11</sup> is a conjugated group, as a pH-dependent marking substance for an oil composition comprising a natural and/or synthetic base oil, said one or more compounds of formula IV giving a colour reaction under action of an aqueous solution of protic acid.

20 7. A method for detecting the presence of a marking substance in an oil composition which comprises a major

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amount of a natural and/or synthetic base oil and a detectable level of a marking substance, wherein the oil composition is contacted with a test strip comprising an acidic compound supported thereon, such that said marking substance gives a colour reaction upon contact with the test strip.

8. Method according to Claim 7, wherein the acidic compound is adsorbed on a carrier prior to being supported on the test strip.
9. Method according to Claim 7 or 8, wherein the acidic compound is selected from trichloroacetic acid, hydrochloric acid, sulphuric acid, 4-dodecylbenzene sulphonic acid (DBSA), picric acid and benzene sulphonic acid.
10. Method according to any one of Claims 7 to 9, wherein the oil composition is according to any one of Claims 1 to 5.
11. A test strip as described in the method of any one of Claims 7 to 9.
12. Use of a test strip according to Claim 11, in the method of any one of Claims 7 to 9.

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